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SYNTHESIS OF ORGANOMERCURY NITROCOMPOUNDS REPORT I:
MERCURATION OF AROMATIC AND HETEROCYCLIC COMPOUNDS
BY DITRINITROMETHYLMERCURY

By S. S. Novikov,
T. I. Godovikova et al

- USSR -

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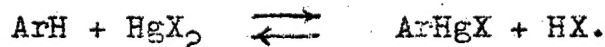
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SYNTHESIS OF ORGANOMERCURY NITROCOMPOUNDS --
 REPORT I. MERCURATION OF AROMATIC AND
 HETEROCYCLIC COMPOUNDS BY DITRINITROMETHYL-
 MERCURY

- USSR -

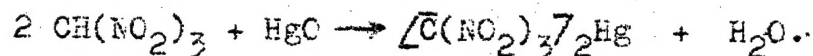
Following is a translation of the article entitled "Sintez rtutnoorganicheskikh nitrosoyedineniy -- Soobshcheniye I. Merkurircvaniye rtutnoy sol'yu trinitrometana aromatischeskikh i geterotsiklicheskh soyedineniy" (English version above) by S. S. Novikov, T. I. Godovikova and V. A. Tartakovskiy in Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk (News of the Academy of Sciences USSR, Department of Chemical Sciences), No 3, Moscow, March 1960, pages 505-512.⁷

The mercuration reaction occupies an important place among the methods of synthesis of aromatic organomercury compounds. The conditions for the reaction vary widely with relation to the structure of the aromatic compound, and both mercuric oxide and its derived salts are used as mercurating agents (1). However, there are no descriptions in the literature of any attempt to use the mercury (II) salts of nitroalkanes as mercurating agents. It could be assumed that the mercury (II) salts of the acidic form of nitroalkanes would be inclined to enter a mercurating reaction according to the general scheme

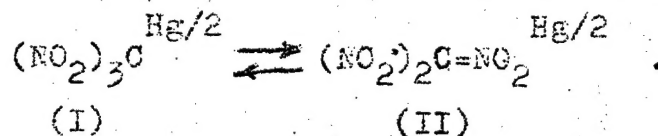


The present work was begun by us with the study of the mercurating ability of ditrinitromethylmercury

as a substance for which the tautomeric conversion into the acidic form occurs with especial ease. Ditrinitromethylmercury was first synthesized by Ley and Kissel (2) by the action of an ethyl ether solution of trinitromethane upon freshly prepared mercuric oxide



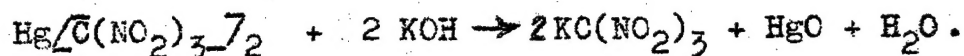
The information available from the literature is related primarily to the ability of this mercury salt to occur in two mutually transforming forms, (2-4)



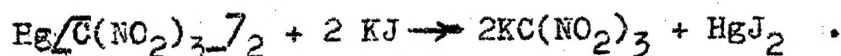
In the crystalline state, as well as in non-polar solvents, ditrinitromethylmercury is an organometallic compound (I). In alcohol this organometallic compound is in equilibrium with its isomeric form (II), which is a derivative of the acidic form of trinitromethane. In very dilute aqueous solutions the mercury salt is completely converted into a derivative of the acidic form.

While investigating the possibility of using the ditrinitromethylmercury salt for the mercuration reaction, we decided to study more extensively its physical and chemical properties. This salt can be obtained, as it was by us, by the reaction of trinitromethane with mercuric oxide, not only in ether but in water and alcohol as well. The freshly prepared mercuric salt decomposes, without melting, at 200-205°. Upon its storing both in the dry state and also in ether solution, partial decomposition of the salt takes place. The solutions in alcohol and water are more stable, and in such solvents the mercuric salt can be stored for several months. Upon applying heat to its butyl ether solution the decomposition of ditrinitromethylmercury that occurs is particularly obvious at temperatures above 100°. As a result of decomposition a precipitate is formed, which is insoluble in organic solvents, water, or dilute mineral acids; at 145-150° it decomposes explosively with the liberation of metallic mercury. The characteristic qualitative reaction of mercurous salts is obtained upon treatment with a dilute aqueous solution of potassium hydroxide, ammonium hydroxide, or potassium iodide.

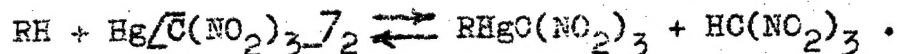
Potassium trinitromethane and mercuric oxide are formed in the reaction of KOH with the mercuric salt of trinitromethane



Potassium iodide decomposes only very slowly (in the course of two weeks) ditrinitromethylmercury according to the equation

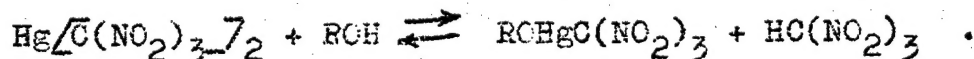


The present work included the investigation of the action of ditrinitromethylmercury upon a number of aromatic and heterocyclic compounds: benzene, toluene, anisole, dimethylaniline, furan, thiophene, pyrrole, and N-methylpyrrole. It was found that, upon the mercuriation of these compounds by ditrinitromethylmercury (with the exception of the pyrroles), mono-mercurated derivatives are formed with a yield of 30 - 70 %



The mercuriation of benzene and toluene is carried out with an excess of these reagents at 80° in the course of 3 - 5 hours; anisole, aniline, and N-dimethylaniline in alcohol at room temperature (in the case of anisole, at 80°); furan and thiophene -- in moist ether at room temperature. In the mercuriation of anisole and toluene o- and p-isomers were isolated.

Ditrinitromethylmercury does not react with benzol in either aqueous or alcoholic solutions. This fact, apparently, could be explained as due to the existence of an equilibrium in the presence of these solvents between ditrinitromethylmercury and its hydroxide (alkoxide) along with the formation of the acidic form (5)

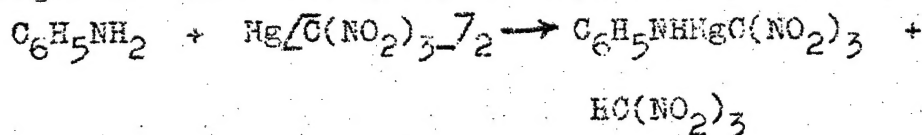


Free trinitromethane, formed during this process, is a strong acid (6) and retards the progress of the benzene mercuriation reaction, which, as is known (1), requires very specific conditions. On the other side, the appearance of a faint yellow coloration during the dissolution of ditrinitromethylmercury in moist benzene (Note 7)

moist benzene is used in the reaction) indicates the formation of the acidic form of the mercuric salt, which is in fact the mercurating agent.

In alcoholic solution, the presence of free trinitromethane does not interfere with the reaction between ditrinitromethylmercury and aniline, dimethylaniline, or anisole, because amino- and oxy-derivatives of benzene react easily with mercuric salts (1). The mercuration of furan or thiophene by ditrinitromethylmercury in aqueous or alcoholic solutions gives rise to a considerable amount of resinous matter in the reaction mixture, and the yield does not exceed 5 - 10 %; carrying out the reaction in moist ether solution results in a yield of ~30 % of mono-mercured compounds.

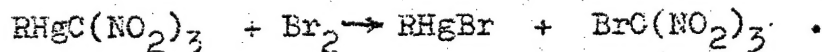
Attention is called to the fact that upon the mercuration of aniline by ditrinitromethylmercury, a hydrogen of the amino group is replaced by mercury



with the simultaneous mercuration of the aniline ring by the acetate of mercury (7). In the case of N-dimethylaniline the reaction product is p-trinitromethylmercurodimethylaniline.

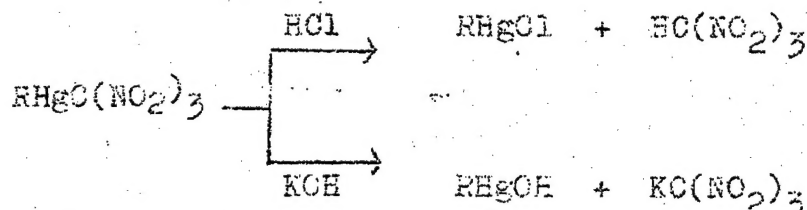
The mercuration products formed, after removal of solvent, are carefully washed with water to remove an excess of ditrinitromethylmercury and free trinitromethane, which latter compound was formed during the reaction. It is interesting to note, that under the mercuration conditions selected by us the formation of poly-mercured compounds was not observed. The mono-mercured compounds obtained dissolve readily in alcohol (except for the derivatives of aniline and dimethylaniline), in acetone, and in ether, but are not soluble in water, and almost all the mono-mercured compounds melt with decomposition.

Trinitromethylmercuroalkanes form, by the action of bromine in an alcohol solution the corresponding mercurobromides and bromotrinitromethane

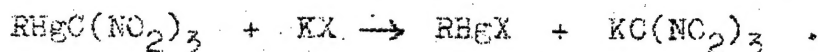


Concentrated hydrochloric acid converts the trinitromethylmercuroalkanes into mercurochlorides and the

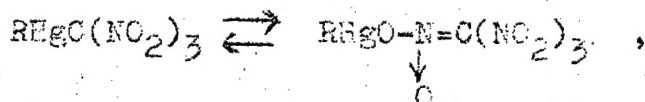
alkali hydroxides -- into the corresponding mercurio-alkoxides



The confirmation of the structures of the synthesized organomercury compounds was accomplished by replacing the trinitromethyl radical by a halogen, in the reaction of a potassium halide with the products of mercuration according to the scheme



The ultraviolet spectra of the compounds that were synthesized by us, when photographed in polar and non-polar solvents, differ sharply and coincide with the spectra obtained by Hantzsch for ditrinitromethylmercury in the corresponding solvents (3). This circumstance allows us to assume that the products of mercuration, as well as the ditrinitromethylmercury, can exist, depending upon the nature of solvent, in two tautomeric forms

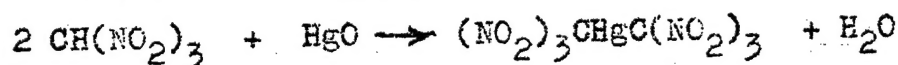


and in the crystalline state they are true organometallic compounds, $\text{REHgC(NO}_2)_3$.

The mercuration of pyrrole and N-methylpyrrole by ditrinitromethylmercury is carried out in ether or in alcohol at -10° . The reaction products, insoluble in any solvent, decompose upon heating without melting. As is known, the action of mercuric chloride on pyrrole and its homologues leads to the formation of insoluble substance of the structure of $(\text{pyrrole})_2\text{Hg(HgCl}_2)_4$ (8). It is probable that in our case the reaction goes in the same direction.

EXPERIMENTAL PART

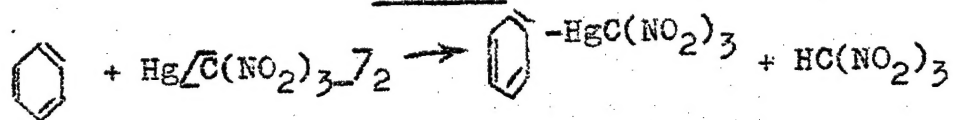
Synthesis of ditrinitromethylmercury



To 16 gm (0.07 M) of freshly prepared mercuric oxide in 50 ml of ether [See Note] small portions of an ether solution of 20 gm of trinitromethane (0.13 M) are added, which addition is accompanied by an increase of temperature up to 30°. The reaction mixture is stirred for 15 minutes, and then the ether solution is filtered free of the unreacted mercuric oxide. Ether is evaporated and ditrinitromethylmercury appears in the form of a precipitate of viscous, light-yellow oil, which crystallizes within 5 - 6 hours. The crystals are separated from the oil by a porous filter; the decomposition temperature is 200 - 205°; and the yield is 26.5 gm (80 % of the theoretical yield). Ditritromethylmercury dissolves readily in water, alcohol, chloroform, acetone, benzene, ethyl acetate, and acetic acid, but is insoluble in petroleum ether, hexane, and isooctane.

([Note] The quantitative yield of ditrinitromethylmercury can be obtained from aqueous or alcoholic solutions.)

The reaction of ditrinitromethylmercury with benzene

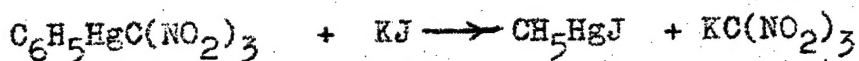


Five gm of ditrinitromethylmercury is dissolved in 20 ml of benzene and three ml of ether [See Note]. The solution is filtered to remove the negligible amounts (50 - 100 mg) of inorganic byproducts (products of the decomposition of the mercuric salt) and is kept upon a water bath for five hours at a temperature of 85 - 90°. After the heating is completed, the hot solution is filtered; upon cooling, there precipitates colorless crystals of trinitromethylmercurobenzene. The crystals are filtered off and washed a few times with water. An additional 0.5 gm of trinitromethylmercurobenzene can be obtained upon removal of benzene from the mother liquor at a pressure of 250 mm down to 5 - 10 ml of the

solution. The total yield is 2.5 gm, which is 58.5 % of the theoretical. After recrystallization from CCl_4 two gm of trinitromethylmercurobenzene are obtained; its melting point is 146° . These values were found: C -- 19.96 %; 19.90 %; H -- 1.33 %; 1.30 %; N -- 9.71 %; 9.71 %. $\text{C}_6\text{H}_5\text{HgC}(\text{NO}_2)_3$. These values were calculated: C -- 19.70 %; H -- 1.18 %; and N -- 9.85 %.

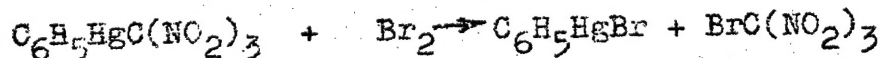
For a confirmation of the structure of the trinitromethylmercurobenzene that was obtained the following reactions were carried out.

The reaction of trinitromethylmercurobenzene with potassium iodide



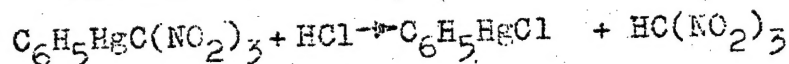
To a solution of one gm of $\text{C}_6\text{H}_5\text{HgC}(\text{NO}_2)_3$ in five ml of acetone there is added a hot solution of 0.4 gm of KI in five ml acetone; there is formed immediately silvery crystals of mercurobenzene iodide, which is filtered and re-crystallized from benzene: m. p. -- 265° . The literature data (9): m. p. -- 266° .

The reaction of trinitromethylmercurobenzene with bromine



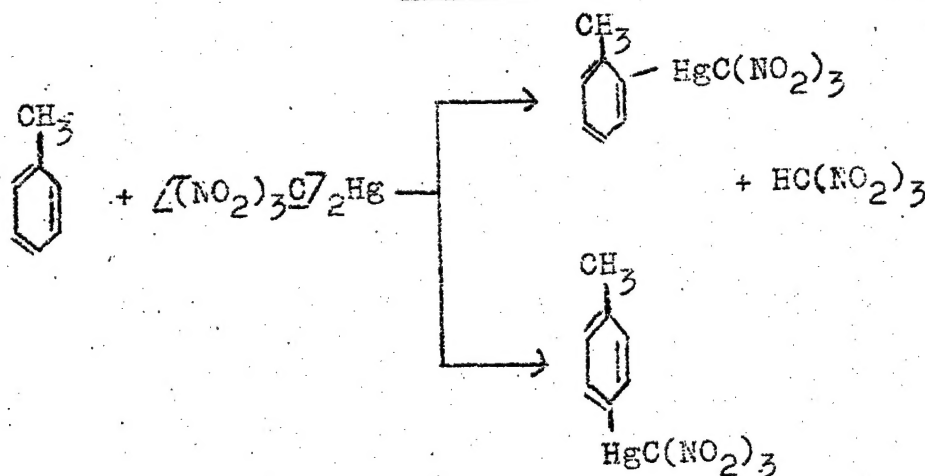
To a solution of three gm of $\text{C}_6\text{H}_5\text{HgC}(\text{NO}_2)_3$ in 15 ml of chloroform a solution of bromine in CH_2Cl_2 is slowly added at room temperature until the non-fading color of bromine appears. As a measure of the addition of bromine there is a precipitation of mercurobenzyl bromide; it is filtered and re-crystallized in a mixture of alcohol and benzene (1:1); the melting point is 275° . Data from the literature (10): m. p. 275° . From the chloroform solution it is also possible to extract bromotrinitromethane with a boiling point of 69° (at 20 mm); $n_D^{20} = 1.4899$. The data from the literature gives: $n_D^{20} = 1.4900$. (11) b.p. -- 68° (at 20 mm); $n_D^{20} = 1.4900$.

The reaction of trinitromethylmercurobenzene
with concentrated hydrochloric acid



One gm of $\text{C}_6\text{H}_5\text{HgC}(\text{NO}_2)_3$ is heated for five minutes with concentrated HCl . During the heating mercurophenyl chloride is formed, which is filtered, washed with water and re-crystallized in alcohol: m.p. -- 252° . The literature data (12): m.p. -- 252° .

The reaction of trinitromethylmercury with
toluene



The mercuration of toluene is carried out under the same conditions as for the mercuration of benzene. The reaction mixture is heated for three hours, after which it is filtered and the excess of toluene is distilled off at 10 mm of pressure to a remaining volume of ~ 5 ml. The precipitated crystals of p-trinitromethylmercury are separated out, washed with water, air-dried, and re-crystallized in carbon tetrachloride; m. p. -- 149° . These values were found: C -- 21.45 %; 21.77 %; H -- 1.70 %; 1.73 %; N -- 9.49 %; 9.59 %.

$\text{C}_8\text{H}_7\text{O}_6\text{N}_3\text{Hg}$. These values were calculated: C -- 21.75 %; H -- 1.59 %; and N -- 9.51 %.

After adding water to the toluene solution colorless crystals of o-trinitromethylmercury are separated out with a m. p. of 126° . The total yield is 51.5 % of the theoretical. The values found: C -- 21.98 %; 21.94 %;

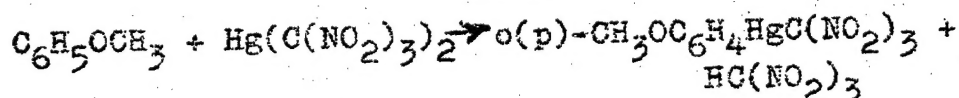
H -- 1.79 %; 1.76 %; N -- 9.65 %; 9.79 %. $C_8H_7O_6N_3Hg$.
 The values calculated: C -- 21.75 %;
 H -- 1.59 %; and N -- 9.51 %.

The reaction of o- and p-trinitromethyltolylmercury with potassium chloride



When an alcoholic solution of $p-CH_3C_6H_4HgC(NO_2)_3$ is treated with an equimolecular amount of KCl, crystals of p-tolylmercury chloride precipitate. The melting point, after recrystallization from alcohol, is 238° . The literature data (13): m. p. -- $238 - 239^\circ$. In the reaction between an alcoholic solution of $o-CH_3C_6H_4HgC(NO_2)_3$ with KCl a precipitate is not formed since the corresponding chloride is readily soluble in alcohol. After the removal of solvent, o-tolylmercury chloride is separated out and recrystallized from 50 % alcohol; m. p. -- $145 - 146^\circ$. The literature data (14): m. p. -- $145-146^\circ$.

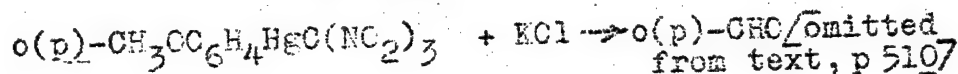
The reaction of ditrinitromethylmercury with anisole



A solution of five gm of ditrinitromethylmercury in seven ml of alcohol containing two ml of anisole is heated for 30 minutes on a water bath up to boiling. After the removal of alcohol, there remains a light-yellow oil, which crystallizes within 2 - 3 hours completely. The crystals are washed with water and air-dried. As a result of the reaction, a mixture of o- and p-trinitromethylanisylmercury is formed; the isomers are separated by recrystallization from 50 % alcohol, in which the p-isomer is easily soluble. The melting point of o-trinitromethylanisylmercury, after its recrystallization from CCl_4 is 114° (with decomposition); the p-isomer had a melting point, after recrystallization from CCl_4 of 101° (with decomposition). The total yield is 41 % of the theoretical. These values were found: C -- 20.68 %; 29.69 %; H -- 1.36 %;

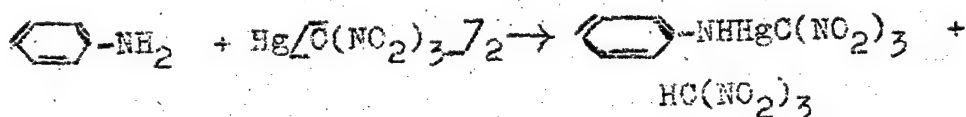
1.46 %; and N -- 8.72 %; 8.83 %. $C_8H_7O_7N_3Hg$. These values were calculated: C -- 20.99 %; H -- 1.69%; and N -- 9.18 %.

The reaction of o- and p-trinitromethylanisyl-mercury with potassium chloride



The reaction between o- and p- $CH_3OC_6H_4HgC(NO_2)_3$ with KCl is conducted under the same conditions as for the corresponding derivatives of toluene. In the case of the p-derivative the chloride obtained has a melting point of 239° (from alcohol); and the c-chloride -- $174 - 175^\circ$ (from 50 % alcohol). The literature data for the p-isomer gives a melting point of 239° (15); the melting point of o-anisylmercury (16) is $174-175^\circ$.

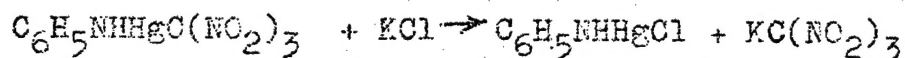
The reaction of ditrinitromethylmercury with aniline



To a solution of 2.5 gm of aniline (0.027 M) in 10 ml of alcohol a solution of five gm of ditrinitromethylmercury in 15 ml of alcohol is added. The yellow precipitate appears immediately, which is filtered off and washed with water, alcohol, and ether [See Note 7]. The product of the reaction if heated decomposes without melting at 117° ; the yield is 2.6 gm (59 % of the theoretical). These values were found: C -- 18.96 %; 19.00 %; H -- 1.67 %; 1.76 %; $C_7H_6O_6N_4Hg$. These values were calculated: C -- 18.98 %; H -- 1.36 %.

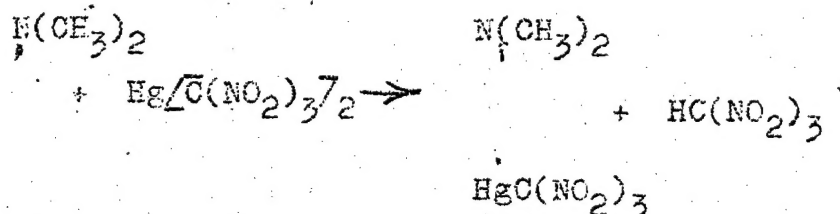
(Note 7 Alcohol is used to remove the trinitromethylaniline, which is easily obtained by the action of equimolecular quantities of trinitromethane and aniline in ether. The salt is a yellow crystalline substance, insoluble in ether, and in cold water, but easily soluble in alcohol; at 130° it decomposes violently.)

The reaction of N-trinitromethylmercurioaniline
with potassium chloride



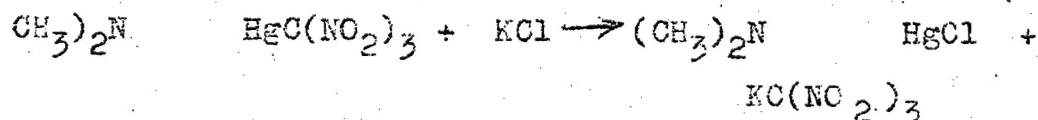
A solution of 0.3 gm of $\text{C}_6\text{H}_5\text{NHHgC}(\text{NO}_2)_3$ in 25 ml of alcohol is heated to boiling and an alcoholic solution of 0.06 gm of KCl is added. The heating is continued for 30 minutes, during which time a powdery precipitate is formed. The product obtained is identical in properties to N-chloromercurioaniline, as described in the literature (17).

The reaction of ditrinitromethylmercury with
N-dimethylaniline



To a solution of five gm of ditrinitromethylmercury in 15 ml of alcohol an alcoholic solution of 4.8 gm of dimethylaniline (1:1) is added. There is an immediate appearance of yellow precipitate, which is filtered off and carefully washed with alcohol to remove the trinitromethyl salt of dimethylaniline. The reaction product, trinitromethylmercuriodimethylaniline is insoluble in water, alcohol, and ether, but is readily soluble in acetone. The substance is purified by adding water to its acetone solution; it decomposes without melting at 110° . The product of mercuriation is unstable for storage.

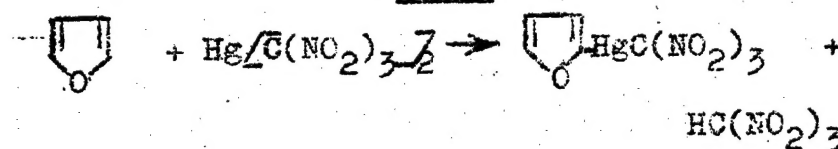
The reaction of p-trinitromethylmercuriodimethylaniline with potassium chloride



On the addition of an aqueous solution of 0.07 gm of KCl to 0.4 gm of p-trinitromethylmercuriodimethyl-

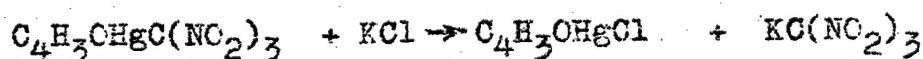
aniline in 10 ml of acetone, white crystals of p-chlor-
omercurodimethylaniline are precipitated, which are re-
crystallized from chloroform; m. p. -- 223 - 225° (with
decomposition). The literature data (15): m. p. --
225° (with decomposition)

The reaction of ditrinitromethylmercury with
furan



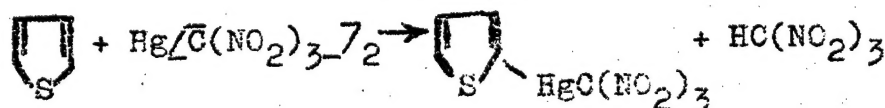
To an ether solution of five gm of ditrinitrometh-
ylmercury 3.7 gm (six-fold excess) of freshly prepared
furan is added. In half an hour the reddish-colored
reaction mixture is poured into 30 ml. of water. After
the removal of ether and the excess furan, trinitro-
methylmercurofuran appears as a viscous oil, which crys-
tallizes quickly. The crystals are washed with water,
air-dried and recrystallized from CCl_4 ; the temperature
of decomposition is 120°; the yield is 25% of the theor-
etical. These values were found: C -- 14.79%; 14.71%;
H -- 0.85%; 1.00%; and N -- 9.98%; 10.03%.
 $\text{C}_5\text{H}_3\text{O}_2\text{N}_3\text{Hg}$. These values were calculated: C -- 14.38%;
H -- 0.76%; and N -- 10.01%.

The reaction of trinitromethylmercurofuran with
potassium chloride



To an alcoholic solution of $\text{C}_4\text{H}_3\text{OHgC}(\text{NO}_2)_3$ an
equivalent amount of KCl is added. The crystalline pre-
cipitate of α -furylmercury chloride forms immediately,
which, after recrystallization, exhibits a melting
point of 151°. The literature data (18): 151°.

The reaction of ditrinitromethylmercury with
thiophene



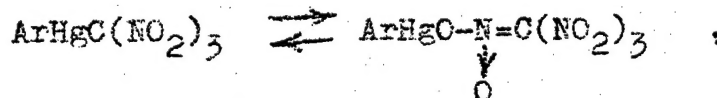
The mercuration of thiophene by ditrinitromethylmercury is conducted in the same manner as for furan. Trinitromethylmercurothiophene, after recrystallization from CCl_4 , had a melting point of 115° ; the yield is 28% of the theoretical. These values were found: N -- 9.75%; 9.87%. $\text{C}_5\text{H}_3\text{O}_6\text{N}_3\text{HgS}$. This value was calculated: N -- 9.68%.

The reaction of ditrinitromethylmercury with pyrrole and with N-methylpyrrole

The reaction with equimolecular amounts of ditrinitromethylmercury and pyrrole (or N-methylpyrrole) in an alcoholic solution at -10° leads to a formation of a yellow precipitate, which must be quickly separated from the reaction mixture, which contains trinitromethane, because the product becomes resinous under the action of acids. The substance obtained decomposes at 122° (N-methylpyrrole decomposes at 117°); it does not dissolve either in water nor in organic solvents. Both compounds give the Ehrlich reaction.

Conclusions

1. Ditrinitromethylmercury is a new mercurating agent for a number of aromatic and heterocyclic compounds.
2. Aromatic and heterocyclic compounds are mercurated by ditrinitromethylmercury relatively easier than by the other salts of mercury.
3. Trinitromethylmercuroalkanes are able to exist in two tautomeric forms



and in the crystalline state are true organometallic compounds.

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